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THE ROLE OF ADSORPTION IN THE CATALYTIC PARA-ORTHO HYDROGEN CONVERSION

HERBERT R. LANDER, JR.

TECHNICAL REPORT AFAPL-TR-66-142

JANUARY 1967

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THE ROLE OF ADSORPTION IN THE CATALYTIC PARA-ORTHO HYDROGEN CONVERSION

HERBERT R. LANDER, JR.

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FOREWORD

This report was prepared as part of the in-house research on unconventional aerospace fuels by the Fuels, Lubrication, and Hazards Branch, Support Technology Division of the Air Force Aero Propulsion Laboratory.

This analysis was performed under Project 3048, Aerospace Fuels, Task 304802, Unconventional Fuels.

This report was submitted by the author 7 December 1966.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Arthur V. Churchill
ARTHUR V. CHURCHILL,
Chief, Fuels, Lubrication and Hazards Branch
Support Technology Division

ABSTRACT

Adsorption isotherms of the form

$$C_A = \frac{L' K' (p_A)^n}{1 + K' (p_A)^n}$$

were determined for two para-ortho-hydrogen conversion catalysts, hydrous ferric oxide gel and nickel oxide silicate, at temperatures from 63°K to 196°K and at pressures from 1 to 10 atmospheres.

For the catalysts studied, Langmuir's isotherm holds at 194.6°K, while at lower temperatures (approximately 60-90°K), the adsorption mechanism appears to be one where two molecules are adsorbed on five effective centers.

(Distribution of this abstract is unlimited)

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SECTION I

INTRODUCTION

GENERAL INFORMATION

The existence of the para and ortho modifications of molecular hydrogen is a direct result of the orientation of the nuclear spins associated with the hydrogen atoms of the molecule. In molecular hydrogen, the nuclear spins of the individual atoms are oriented either in the same direction (parallel), which corresponds to the ortho modification, or in the opposite direction (antiparallel), which corresponds to the para modification. These two orientations of nuclear spins are responsible for the differences in the magnetic and the thermal properties of ortho and para modifications of molecular hydrogen. An equilibrium, which is a function of temperature, exists between the two forms.

Under equilibrium conditions, shown graphically in Figure *1, the para-hydrogen concentration in the pure hydrogen gas varies from essentially 100% para at 36°R to approximately 25% para at 270°R. Since the para to ortho-hydrogen conversion is endothermic in this temperature range (339 calories per mole), certain additional low temperature refrigeration is available from the conversion. Interest in the conversion of hydrogen stems from the heat of conversion when the reaction proceeds at low temperatures.

Many of the next generation of aerospace vehicles will use hydrogen as a fuel or propellant. At high flight speeds, the problems associated with cooling air-breathing aircraft engines and other parts will become critical. Problems will be encountered in cooling the walls of the combustion chamber and the exhaust nozzle. The hydrogen fuel will be the most logical reservoir available to absorb heat and thereby provide the critically needed cooling capacity. In many engines under consideration, the hydrogen must be vaporized and superheated in order to obtain sufficient heat-absorbing capacities per pound of fuel. If the para-ortho shift of the hydrogen could be obtained below a temperature of 270°R, the effective heat sink capacity

of hydrogen would be greatly increased, and the required size of the heat exchanger could be reduced.

The relative enthalpies of para, equilibrium, and normal hydrogen are shown in Figure 2. The differences in the enthalpies of hydrogen of the various compositions represent the enthalpy change due to conversion. If the hydrogen is used in a refrigeration circuit which does not contain a conversion catalyst, the temperature-enthalpy path will follow the para curve. However, if a conversion catalyst is included in the system, causing the temperature-enthalpy path to follow the equilibrium curve, significantly greater quantities of refrigeration can be provided by the hydrogen at low temperatures. The successful application of this conversion could increase payload because of reduction in the weights of heat exchangers. The strategic incorporation of this concept in heat exchanger equipment would alleviate "pinch-point" areas by increasing available refrigeration and, therefore, the driving force which causes the flow of heat.

Low-temperature heterogeneous catalysis was considered the most promising technique for effecting the para-ortho shift of hydrogen.

Early studies involved the characterization of the conversion catalysts for use in the production of a large quantity of liquid para-hydrogen. In this process, normal hydrogen (equilibrium hydrogen at standard temperature contains approximately 25% para-hydrogen and 75% ortho-hydrogen) is converted to the corresponding equilibrium hydrogen (approximately 100% para-hydrogen) at liquid hydrogen temperatures (approximately 36°R). This process step is included in the production of liquid hydrogen, since failure to convert the normal hydrogen to the equilibrium concentration would result in the conversion occurring slowly during storage. Since this particular reaction (normal to 99.79% para-hydrogen) is exothermic with a

*Illustrations and tables are in the appendix.

heat release of 226 BTU/lb, the liquid hydrogen would boil away even if it were stored in a perfectly insulated container. For this reason, the conversion from ortho-hydrogen to para-hydrogen is made during the production cycle, and the liberated heat is taken away at this time. Chromium oxide supported on alumina was found to be effective for this conversion, however, a systematic study was undertaken to find materials which might be more effective.

Various metallic oxides such as cerium oxide, ferric oxide, neodymium oxide, and manganese dioxide, both supported and unsupported, were studied. Unsupported hydrous ferric oxide proved to be the most effective conversion catalyst of those studied. A space velocity of 330 STP/minute was achieved with 1/8-inch pellets of this material (Reference 3).

In early 1960, the U. S. Air Force, with its increasing interest in the use of hydrogen as an air-breathing engine propellant, recognized the intriguing possibilities of recovering the available refrigeration from para-hydrogen fuel and initiated a program to develop catalysts (at Air Products and Chemical Inc.) to obtain additional cooling from the para-ortho shift. This work was carried out under contract AF33(616)-7506 and later under contracts AF33(657)-10333 and AF33(615)-1316. The objectives of the investigation were to determine the parameters that effect the shift of para-hydrogen to ortho-hydrogen and to develop a catalyst for speeding the shift toward the equilibrium ratio at low temperatures. The hydrous ferric oxide gel developed for the ortho to para hydrogen shift in commercial plants was found to be effective also for the desired para to ortho hydrogen shift and was chosen as a baseline in the study.

According to theories formulated, there are two fundamental methods of inducing an ortho-to-para or para-to-ortho transition. One method consists of dissociating the hydrogen molecules and allowing the atoms to recombine. When dissociated, the two atomic nuclei no longer are oriented with respect to nuclear spins. Upon reassociation, the molecules are formed according to the equilibrium energy distribution determined by the temperature. The other method involves the interaction between an inhomogeneous magnetic field and the magnetic field associated with the nuclear spin of the hydrogen nuclei. The dissociation or chemical mechanism is catalyzed by any method which is capable of producing hydrogen atoms or at least of destroying the molecular bond between the two nuclei. The magnetic or physical mechanism is catalyzed by any inhomogeneous magnetic field of molecular dimension.

Air Products and Chemicals Inc. developed a nickel oxide silicate catalyst which was 10.5 times more active on a weight basis than the standard hydrous ferric oxide gel.*

OBJECTIVES OF REPORT

In this report, the author will attempt to analyze the hydrogen adsorption data tabulated in Reference 5**, for both the advanced nickel oxide silicate catalyst and the commercial hydrous ferric oxide gel. The analyses will be directed toward determining the adsorption isotherm and gaining an understanding of the possible mechanism for the important adsorption step at the low temperatures of interest. The analyses will follow the approach of Koble and Corrigan (Reference 4) in conjunction with adsorption data for pure hydrocarbons. The author has taken the Koble-Corrigan approach to develop an expression for determining the concentration of hydrogen adsorbed at various temperatures and pressures.

*Recent efforts by the contractor have resulted in a nickel oxide catalyst that was 29 times more active, on a weight basis, than the standard.

**From Reference 5 the data used was equilibrium pressure in atmospheres and volume adsorbed (STP) ml/gm (ca*) which are shown in Tables I through VIII in this technical report.

SECTION II

PROCEDURE FOR DETERMINING THE CONCENTRATION OF ADSORBED HYDROGEN AT VARIOUS TEMPERATURES AND PRESSURES

In Reference 4 a general form for an adsorption isotherm was formulated and is

$$C_A = \frac{L' K' (p_A)^n}{1 + K' (p_A)^n} \quad (1)$$

where

C_A = concentration of adsorbed gas moles per gram of catalyst

L' = empirical adsorption constant related to the total number of active centers available on the adsorbent

K' = empirical adsorption constant related to the equilibrium constant

n = a constant

p_A = equilibrium pressure of the adsorbed gas

Adsorption data for hydrogen on both the commercial hydrous ferric oxide gel catalyst and the advanced nickel oxide silicate material will be used in conjunction with Equation (1), and the various constants will be determined.

Equation (1) is inverted and rearranged to give

$$\frac{1}{C_A} - \frac{1}{L'} = \frac{1}{L' K'} \left(\frac{1}{p_A} \right)^n \quad (2)$$

The original data were reported in Reference 5 as volume of gas adsorbed, in milliliters at standard conditions, and the equilibrium pressure, in atmospheres, of the hydrogen in contact with the catalyst. The adsorption data for the two catalysts at four different temperatures are presented in Tables V through VIII, together with the manipulations necessary for the later treatment of the data.

The approximation of the constant L' for a given catalyst is given in Figures 3 and 4 for

the standard and advanced materials, respectively. L' is determined from the rectangular plot $1/C_A$ versus $1/p_A$.

Figure 3 is a plot of $1/C_A$ versus $1/p_A$ for three of the four test temperatures for the hydrous ferric oxide gel. The intercept was determined to be 0.025; this value could have ranged from approximately 0.020 to 0.040 according to the data reported. That L' is a constant independent of temperature is demonstrated by Figure 3, where the various isotherms converge on apparently the same intercept.

Figure 4 is a plot of $1/C_A$ versus $1/p_A$ for the hydrogen adsorption on the advanced nickel oxide silicate catalyst. Here, again, the isotherms converge on the same intercept which was determined to be 0.0105. This strengthens the concept that L' is a constant and is independent of temperature.

The quantity $(1/C_A - 1/L')$, from Tables I through VIII, is plotted versus $1/p_A$ on logarithmic coordinates for the four temperatures studied. Figure 5 is the correlation for the commercial hydrous ferric oxide, and Figure 6 is a similar plot for the advanced nickel catalyst. Kohle in Reference 4, recommended that the value of L' be corrected by trial and error until the plot of $\log (1/C_A - 1/L')$ versus $1/p_A$ gave a straight line. This procedure was not followed with this data since the adjustment of L' could not straighten out all of the curves, which indicates that mechanisms were changing with both pressure and temperature.

The isotherms for the adsorption on the catalysts studied are parallel for the 63.16, 77.0, and 87.8°K over a pressure range of approximately 1 to 10 atmospheres; data beyond this region were inconclusive and indicated possible changes in the slopes of the curves.

According to Koble's derivation of Equation (1), n should be either an integer or a fraction composed of small integers. Table IX presents the slopes of the isotherms from Figure 5 for the commercial catalyst and similar data from Figure 6 for the advanced catalyst. These data indicate that the adsorption mechanism changes from the lower temperatures to the higher one for both catalysts tested; in fact, the same type of adsorption seems to be taking place in both catalysts.

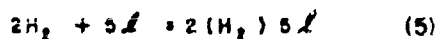
Hydrogen adsorption on both catalysts at 194.6°K follows the Langmuir Isotherm, which has been defined as a specific case of the general adsorption expression (Equation 1), where n is equal to unity. The mechanism for the hydrogen adsorption at this temperature is



where \mathcal{L} is an active center. The expression relating concentration of the adsorbed gas to its equilibrium partial pressure is

$$C_{H_2} = \frac{K' L' P_{H_2}}{1 + K' P_{H_2}} \quad (4)$$

At lower temperatures (60-90°K) for both catalysts tested, the adsorption mechanism resembles the following:



which indicates that two molecules of hydrogen are adsorbed on five active centers. The expression relating the gas concentration adsorbed to the gas partial pressure for this mechanism is

$$C_{H_2} = \frac{K' L' (P_{H_2})^{2/5}}{1 + K' (P_{H_2})^{2/5}} \quad (6)$$

The author postulated that the true mechanism is simply physical adsorption of two molecules on five active centers. It seems unlikely that the mechanism could be chemical dissociation because the near cryogenic temperatures are not compatible with activated adsorption associated with the molecular dissociation mechanisms.

The values of K' were determined from the intercepts of the isotherms with the ordinate at $1/P_A = 1$ from Figures 5 and 6 for the catalytic materials studied. The intercept gives the value of the quantity $1/L'K'$, so that K' can be calculated. These values for the catalysts of interest are given in Table X.

Since K' is related to the true thermodynamic equilibrium constant, a plot of $\log K'$ versus the reciprocal of the absolute temperature should be a reasonably straight line. Figure 7 is a plot of this information for the catalysts of interest. Since the lines are essentially straight, the slope should furnish a useful empirical constant that could be used to predict K' for temperatures other than those measured.

SECTION III

CONCLUSIONS

The adsorption data on the commercially available hydrous ferric oxide gel and the advanced nickel oxide silicate material indicate that the adsorption mechanism is physical. This conclusion is reached primarily because the data were obtained at low temperatures. There are indications also that the adsorption mechanism changes with temperature and possibly with pressure; but, for the temperatures studied (63.16 to 194.6°K), the basic mechanism is physical adsorption. Table XI lists the expressions for the catalysts at the test temperatures.

References 6, 7, and 8 suggested that two mechanisms occurred with para-ortho conversion catalysts. One mechanism is increasingly effective as the temperature is lowered, and the other is increasingly effective as the temperature is raised. Taylor (Reference 9) showed that two types of adsorption occurs. Physical adsorption (Van der Waals) occurs at low temperatures and decreases as the temperature increases while activated, or chemisorption takes place above room temperature and increases as the temperature increases. These theories back the contention of this author that physical adsorption is occurring.

For the catalysts studied, Langmuir's Isotherm holds at 194.6°K, while at lower temperatures (approximately 60-90°K) the adsorption mechanism appears to be one where two molecules are adsorbed on five active centers.

The overall mechanism for the para-to-ortho (or ortho-to-para) shift of hydrogen consists of several consecutive steps. Before

the actual conversion can occur, a hydrogen molecule must diffuse out of the main gas stream to the surface of the catalytic particle and eventually into a small pore of the particle. The molecule must then adsorb onto the surface of the catalyst. We have determined that this step is physical adsorption. Once the molecule is adsorbed, it will migrate along the surface, perhaps passing near an active center. For the para-ortho hydrogen shift, active centers generally are associated with unshared electrons. In strong, inhomogeneous, magnetic fields around such electrons, the restrictions against spontaneous conversion are removed, and the molecule may change to another modification. Finally, the converted molecule must evaporate (physical adsorption to physical desorption) from the adsorbed layer, diffuse along the pore to the outside surface of the particle, and then diffuse into the main gas stream that will carry it from the catalyst chamber. One of these steps, therefore, will control the rate of conversions. Current efforts are aimed at getting sufficient data to determine the exact mechanism and the rate controlling step.

Since the catalytic material desired by the U. S. Air Force for application to possible future aircraft systems must be lightweight, and since the adsorption characteristics at the temperatures of interest are physical in nature, a good catalyst must exhibit certain qualities. Some of these characteristics would be low density, high surface area, high adsorptive capacity, high fraction of the surface area which contains active sites, high site activity, high porosity, and high thermal conductivity.

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APPENDIX

ILLUSTRATIONS AND TABLES

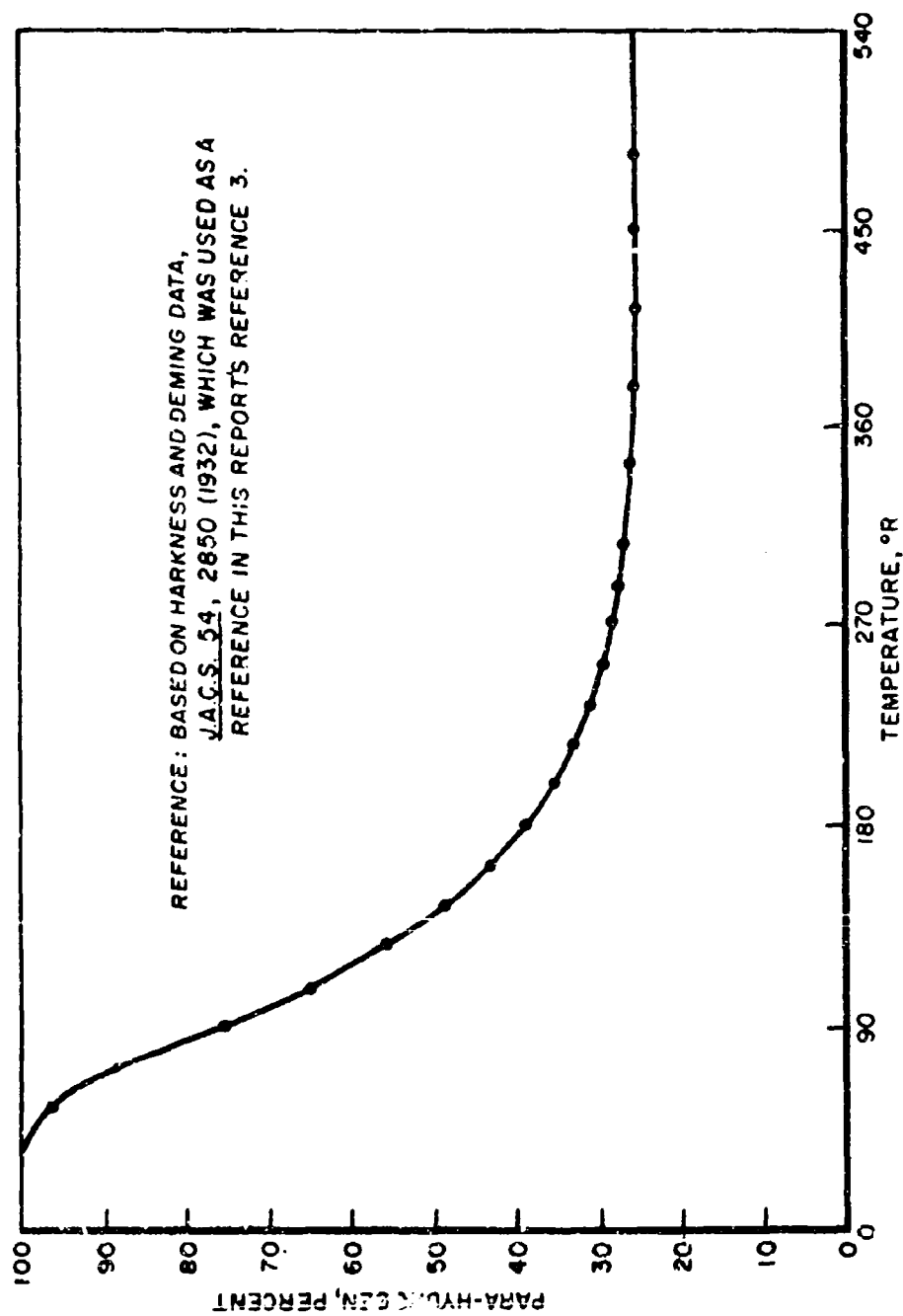


Figure 1. Equilibrium Para-Hydrogen Concentration As a Function of Temperature

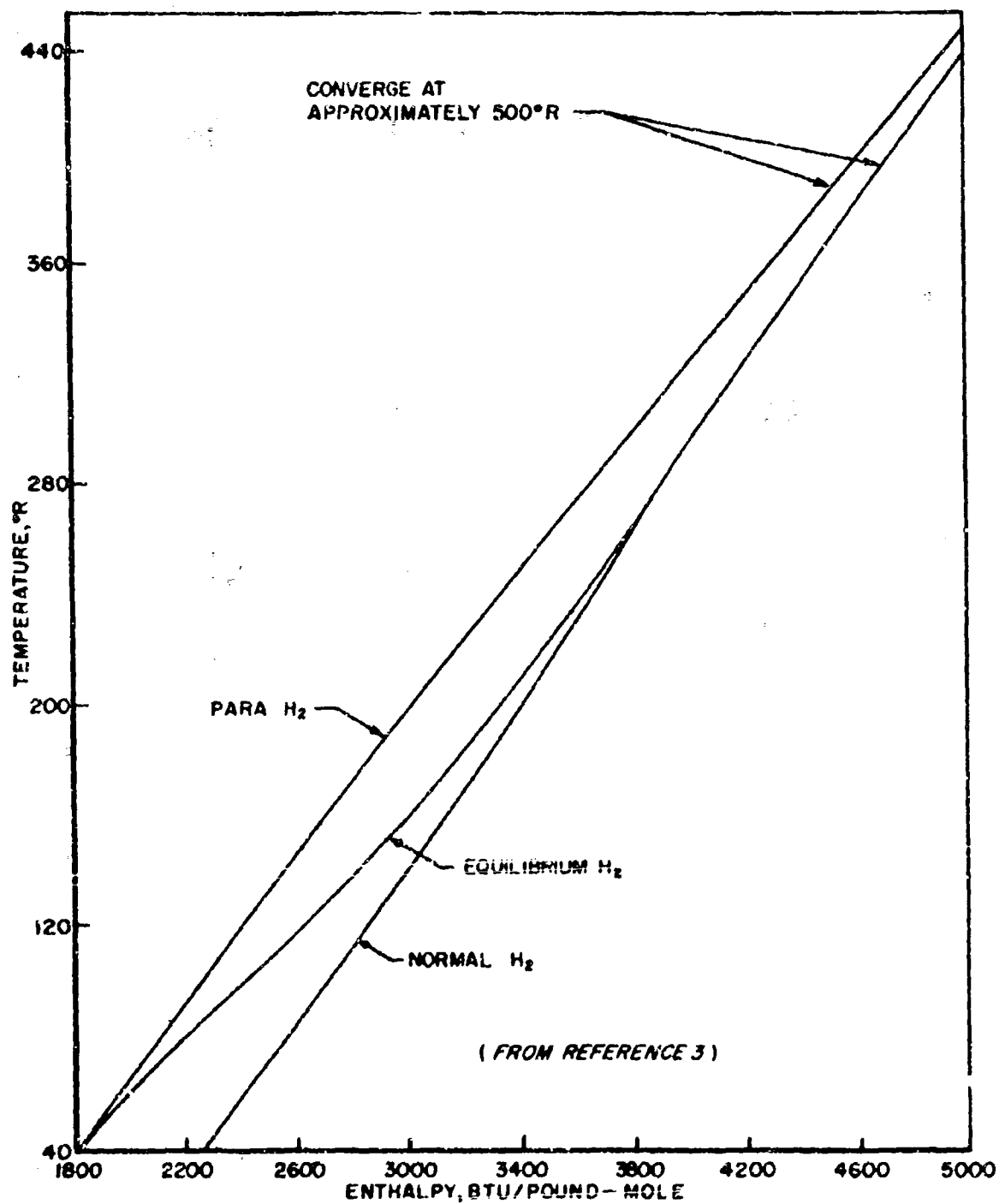


Figure 2. Enthalpy Vs. Temperature for Equilibrium, Para, and Normal Hydrogen at 1500 PSIA.

TABLE I

ABSORPTION DATA FOR HYDROGEN AT 63.16°K WITH
HYDROUS FERRIC OXIDE GEL AS CATALYST

Equilibrium pressure (atms)	Volume adsorbed (STP) ml/gm (cat*)	1/P atm ⁻¹	C _A moles adsorbed moles/gm (cat) x 10 ⁴	1/C _A	1/C _A - 1/L'
0.221	11.6	4.52	5.18	0.193	0.167
1.16	19.1	0.86	8.53	0.117	0.091
2.62	23.4	0.38	10.43	0.096	0.070
3.94	25.7	0.254	11.40	0.088	0.062
5.15	27.3	0.194	12.15	0.082	0.056
6.16	28.3	0.162	12.63	0.079	0.053
9.03	30.9	0.111	13.75	0.073	0.047
11.30	33.3	0.088	14.85	0.067	0.041
15.60	36.7	0.064	16.30	0.061	0.035
19.0	39.0	0.053	17.40	0.057	0.031
22.1	41.2	0.045	18.43	0.054	0.028
24.6	42.9	0.041	19.10	0.052	0.026
26.6	43.5	0.038	19.40	0.051	0.025
28.0	45.3	0.036	20.20	0.050	0.024

Note: *cat is used as abbreviation for catalyst on all tables.

TABLE II

ADSORPTION DATA FOR HYDROGEN AT 77°K WITH
HYDROUS FERRIC OXIDE GEL AS CATALYST

Equilibrium pressure (atms)	Volume adsorbed (STP) ml/gm (cat)	1/P atm ⁻¹	C _A moles adsorbed moles/gm (cat) x 10 ⁴	1/C _A	1/C _A - 1/L'
0.408	6.53	2.45	2.93	0.342	0.316
1.16	11.1	0.86	4.95	0.201	0.175
2.08	14.0	0.48	6.25	0.160	0.134
2.98	15.8	0.335	7.08	0.142	0.116
4.12	17.4	0.243	7.78	0.129	0.103
5.46	19.0	0.184	8.50	0.118	0.092
6.90	20.3	0.145	9.08	0.110	0.084
8.47	21.4	0.118	9.56	0.104	0.078
10.10	22.6	0.099	10.10	0.099	0.073
11.80	23.6	0.085	10.55	0.095	0.069
13.40	24.9	0.075	11.10	0.090	0.064
15.0	26.0	0.067	11.60	0.086	0.060

TABLE III
 ADSORPTION DATA FOR HYDROGEN AT 87.8°K WITH
 HYDROUS FERRIC OXIDE GEL AS CATALYST

Equilibrium pressure (atms)	Volume Adsorbed (STP) ml/gm (cat)	1/P atm ⁻¹	C _A moles adsorbed moles/gm (cat) x 10 ⁴	1/C _A	1/C _A - 1/L'
0.476	4.31	2.10	1.92	0.521	0.495
1.43	8.08	0.70	3.62	0.276	0.250
2.81	11.1	0.355	4.95	0.201	0.175
4.49	13.4	0.223	5.99	0.166	0.140
6.36	15.3	0.158	6.83	0.146	0.120
8.67	16.9	0.115	7.55	0.133	0.107
11.80	18.7	0.085	8.32	0.121	0.095
15.9	20.6	0.063	9.20	0.109	0.083
20.8	22.5	0.048	10.01	0.100	0.074
24.5	23.5	0.041	10.45	0.096	0.070
27.1	24.1	0.037	10.80	0.093	0.067

TABLE IV
 ADSORPTION DATA FOR HYDROGEN AT 194.6°K WITH
 HYDROUS FERRIC OXIDE GEL AS CATALYST

Equilibrium pressure (atms)	Volume adsorbed (STP) ml/gm (cat)	1/P atm ⁻¹	C _A moles adsorbed moles/gm (cat) x 10 ⁴	1/C _A	1/C _A - 1/L'
0.952	0.0123	8.13	0.055	18.20	18.17
2.84	0.494	2.03	0.219	4.56	4.53
4.69	0.742	1.35	0.331	3.01	2.98
6.46	0.998	1.00	0.446	2.24	2.21
8.20	1.23	0.813	0.549	1.82	1.79
10.7	1.58	0.635	0.703	1.42	1.39
15.2	2.19	0.456	0.975	1.025	1.00
20.7	2.96	0.338	1.325	0.755	0.725
27.1	2.98	0.335	1.328	0.751	0.721
30.1	3.79	0.264	1.695	0.590	0.560

TABLE V
 ADSORPTION DATA FOR HYDROGEN AT 63.16°K WITH
 NICKEL OXIDE SILICATE AS CATALYST

Equilibrium pressure (atms)	Volume adsorbed (STP) ml/gm (cat)	1/P atm ⁻¹	C _A moles adsorbed moles/gm (cat) x 10 ⁴	1/C _A	1/C _A ~ 1/L'
0.0	20.4	-	9.10	0.110	0.099
0.306	57.0	3.65	25.40	0.0395	0.0290
1.28	83.4	0.78	37.10	0.0269	0.0164
3.84	106	0.26	47.40	0.0211	0.0106
6.70	117	0.15	52.30	0.0192	0.0087
1.28	84.4	0.78	37.50	0.0267	0.0162
6.00	117	0.167	52.30	0.0192	0.0087
11.2	130	0.089	58.00	0.0172	0.0067
15.7	138	0.064	61.50	0.0162	0.0057
19.3	144	0.052	64.20	0.0156	0.0051
22.1	149	0.045	66.50	0.0150	0.0045

TABLE VI

ADSORPTION DATA FOR HYDROGEN AT 77°K WITH
NICKEL OXIDE SILICATE AS CATALYST

Equilibrium pressure (atmos)	Volume adsorbed (STP) ml/gm (cat)	1/P atm ⁻¹	C _A moles/gm (cat) x 10 ⁴	1/C _A	1/C _A - 1/L'
0	10.5	29.40	4.6	0.217	0.208
0.036	20.2	7.35	9.05	0.1105	0.1309
0.136	34.4	1.61	15.35	0.0654	0.0943
0.986	48.7	0.375	21.30	0.0470	0.0365
2.67	67.9	0.219	29.90	0.0335	0.0230
4.56	77.9	0.158	34.70	0.0288	0.0183
6.33	84.6	0.128	37.80	0.0265	0.0160
7.84	88.9	0.102	39.60	0.0253	0.0148
9.78	93.8	0.082	41.90	0.0239	0.0134
12.10	98.3	0.064	43.90	0.0229	0.0124
15.5	105	0.051	46.90	0.0214	0.0109
19.7	110	0.043	49.10	0.0204	0.0099
23.1	114		50.90	0.0197	0.0092

TABLE VII
 ADSORPTION DATA FOR HYDROGEN AT 87.8°K WITH
 NICKEL OXIDE SILICATE AS CATALYST

Equilibrium pressure (atms)	Volume adsorbed (STP) ml/gm (cat)	1/P atm ⁻¹	C _A moles adsorbed moles/gm (cat) x 10 ⁴	1/C _A	1/C _A - 1/L'
0.221	18.2	4.54	9.12	0.123	0.112
0.816	31.6	1.23	16.05	0.0701	0.0596
2.69	50.4	0.371	22.60	0.0442	0.0337
6.21	66.2	0.161	29.60	0.0338	0.0233
11.05	78.1	0.090	34.90	0.0286	0.0181
4.06	58.3	0.246	26.10	0.0384	0.0279
10.7	77.9	0.094	34.65	0.0288	0.0183
16.5	86.3	0.061	38.60	0.0259	0.0154
21.0	90.7	0.048	40.40	0.0247	0.0142
24.5	92.3	0.041	41.40	0.0241	0.0136
27.0	94.7	0.037	41.70	0.0240	0.0135
28.8	96.1	0.035	42.80	0.0234	0.0129
30.2	96.7	0.033	43.20	0.0231	0.0126

TABLE VIII

ADSORPTION DATA FOR HYDROGEN AT 194 °K WITH
NICKEL OXIDE SILICATE AS CATALYST

Equilibrium pressure (atms)	Volume adsorbed (STP) ml/gm (cat)	1/P atm ⁻¹	C _A moles adsorbed moles/gm (cat) x 10 ⁴	1/C _A	1/C _A - 1/L'
1.38	1.65	0.724	0.647	1.550	1.539
3.67	3.15	0.277	1.405	0.710	0.699
6.12	7.17	0.163	3.200	0.313	0.302
6.56	7.72	0.153	3.450	0.290	0.279
12.8	9.47	0.078	4.24	0.236	0.225
16.1	11.1	0.062	4.96	0.201	0.190
19.5	12.5	0.051	5.59	0.177	0.168
22.8	13.9	0.044	6.19	0.162	0.151
26.3	15.3	0.038	6.84	0.146	0.135
29.6	16.7	0.034	7.45	0.134	0.123

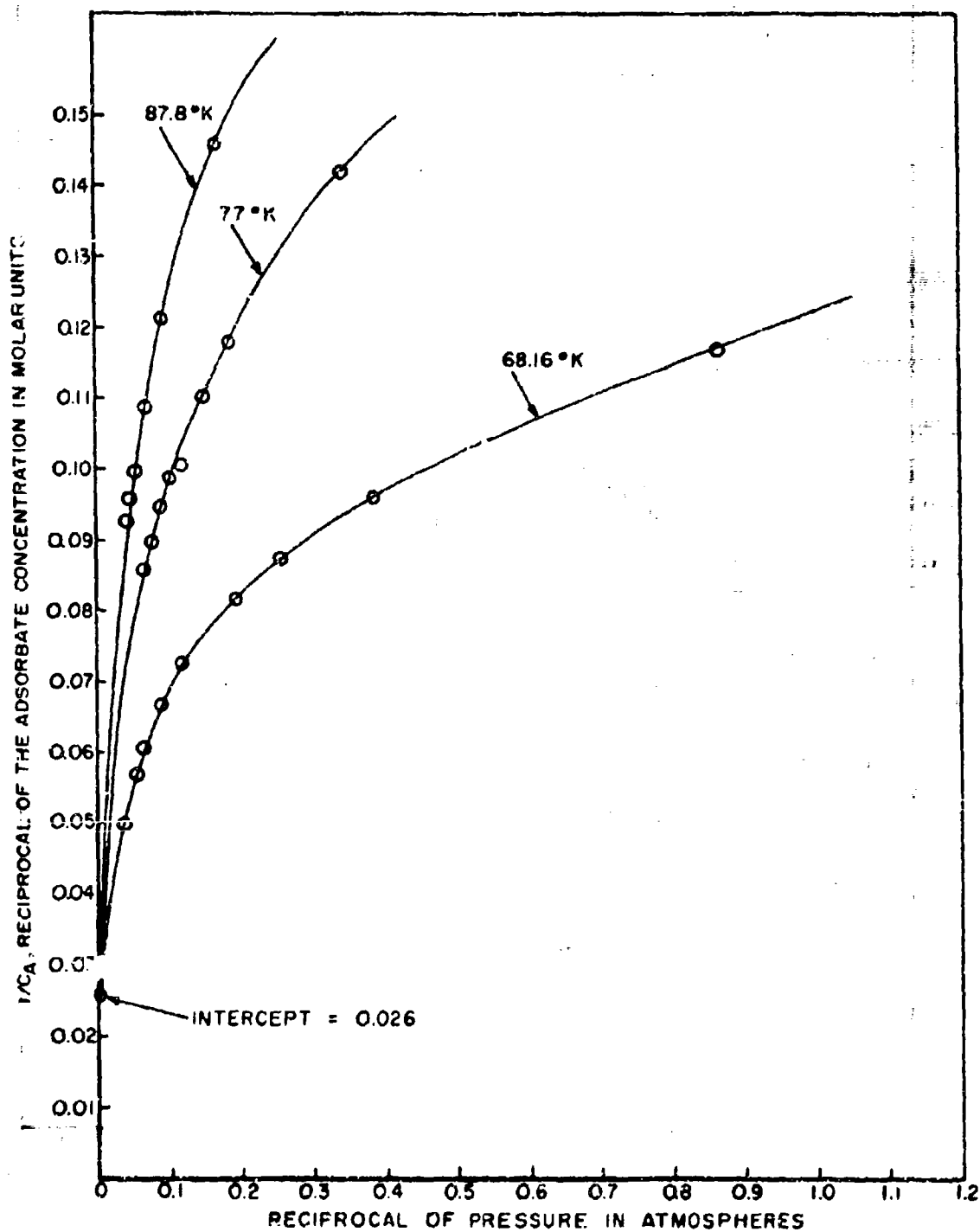


Figure 3. Reciprocal Plot of Isothermal Adsorption Data for Hydrogen on Hydrous Ferric Oxide Gel Catalyst

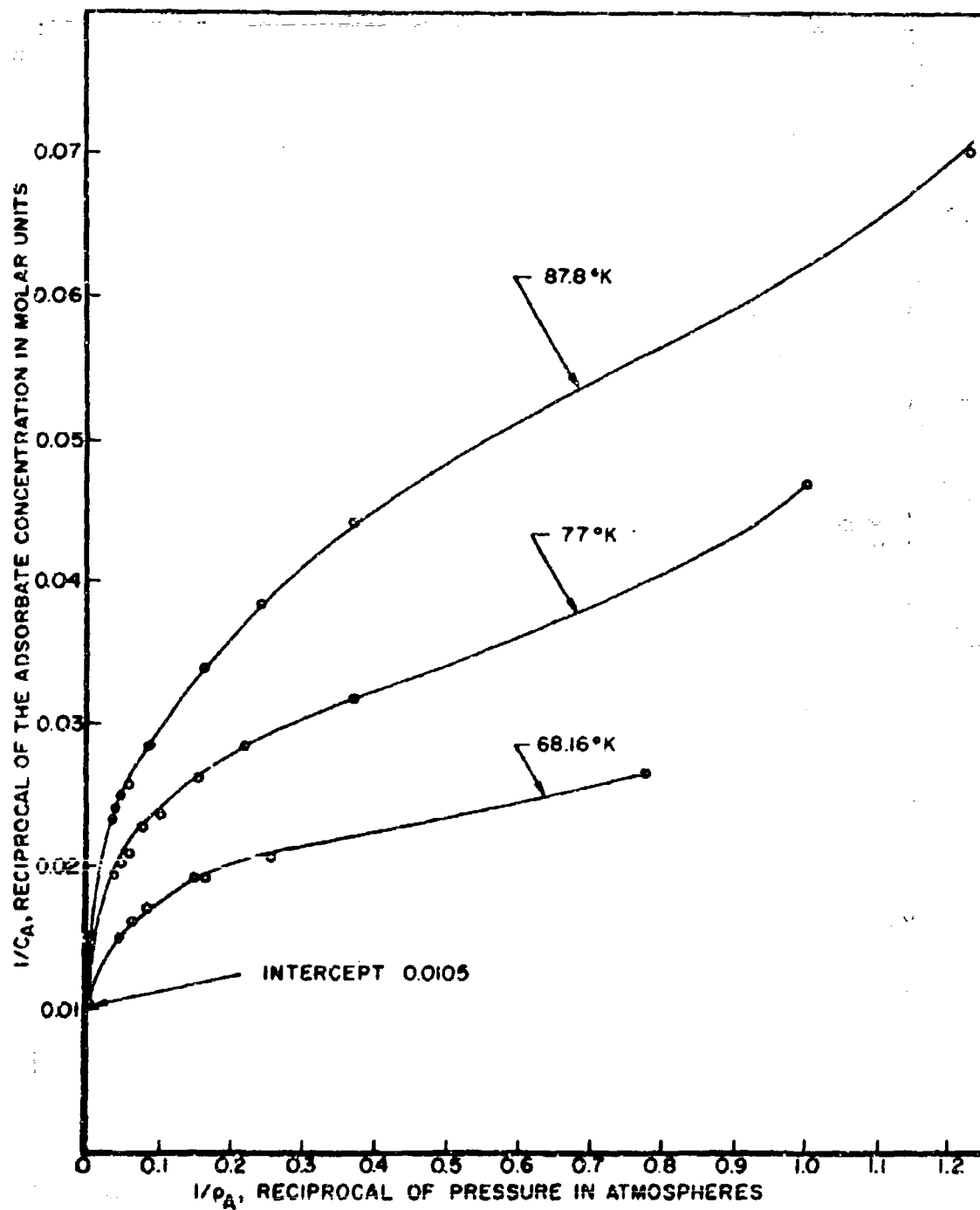


Figure 4. Reciprocal Plot of Isothermal Adsorption Data for Hydrogen on Nickel Oxide Silicate Catalyst

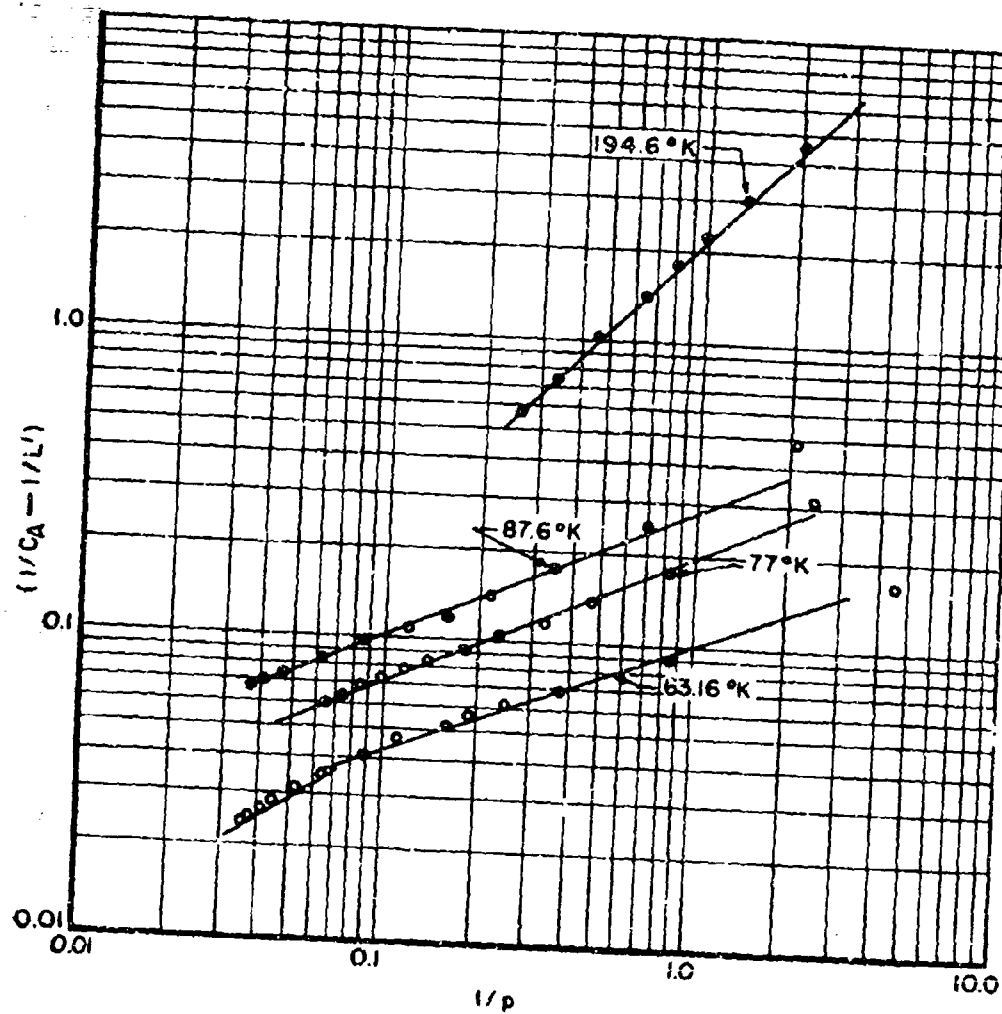


Figure 6. Correlation of Hydrogen on Hydrous Ferric Oxide Gel According to Equation (2)

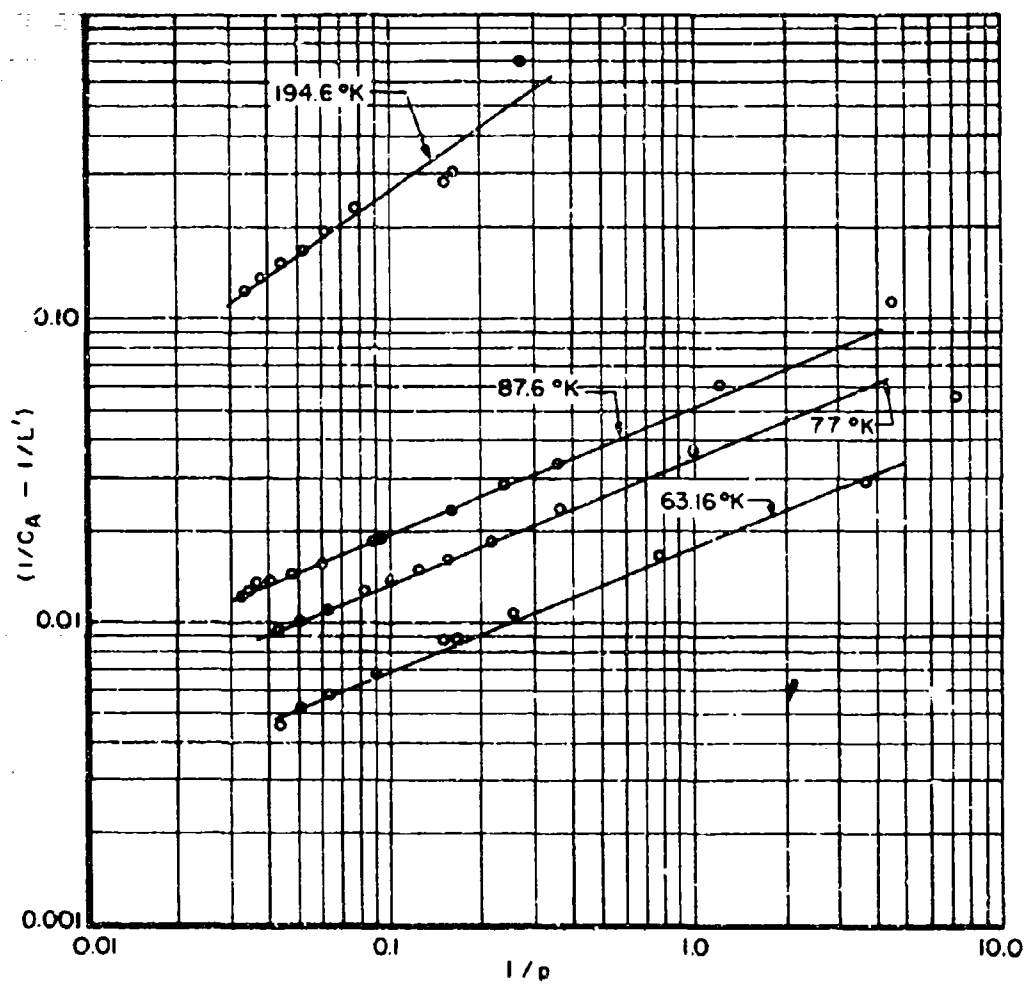


Figure 6. Correlation of Hydrogen on Nickel Oxide Silicate According to Equation (2)

TABLE IX
VALUES OF L' AND n

Hydrogen Adsorption On Hydrous Ferric Oxide Gel -- $L' = 38.46$		
Temperature (°K)	Slope of curve (Figure 5)	Nearest fraction n
63.16°K	0.377	2/5
77°K	0.433	2/5
87.8°K	0.450	2/5
194.6°K	1.000	1
Hydrogen Adsorption On Nickel Oxide Silica -- $L' = 95.24$		
Temperature (°K)	Slope of curve (Figure 6)	Nearest fraction n
63.16°K	0.429	2/5
77°K	0.426	2/5
87.8°K	0.418	2/5
194.6°K	0.960	1

TABLE X
VALUES OF K'

Temperature (°K)	Hydrous ferric oxide	Nickel oxide silicate
63.16	0.260	0.598
77	0.133	0.314
87.8	0.095	0.211
194.5	0.017	0.008

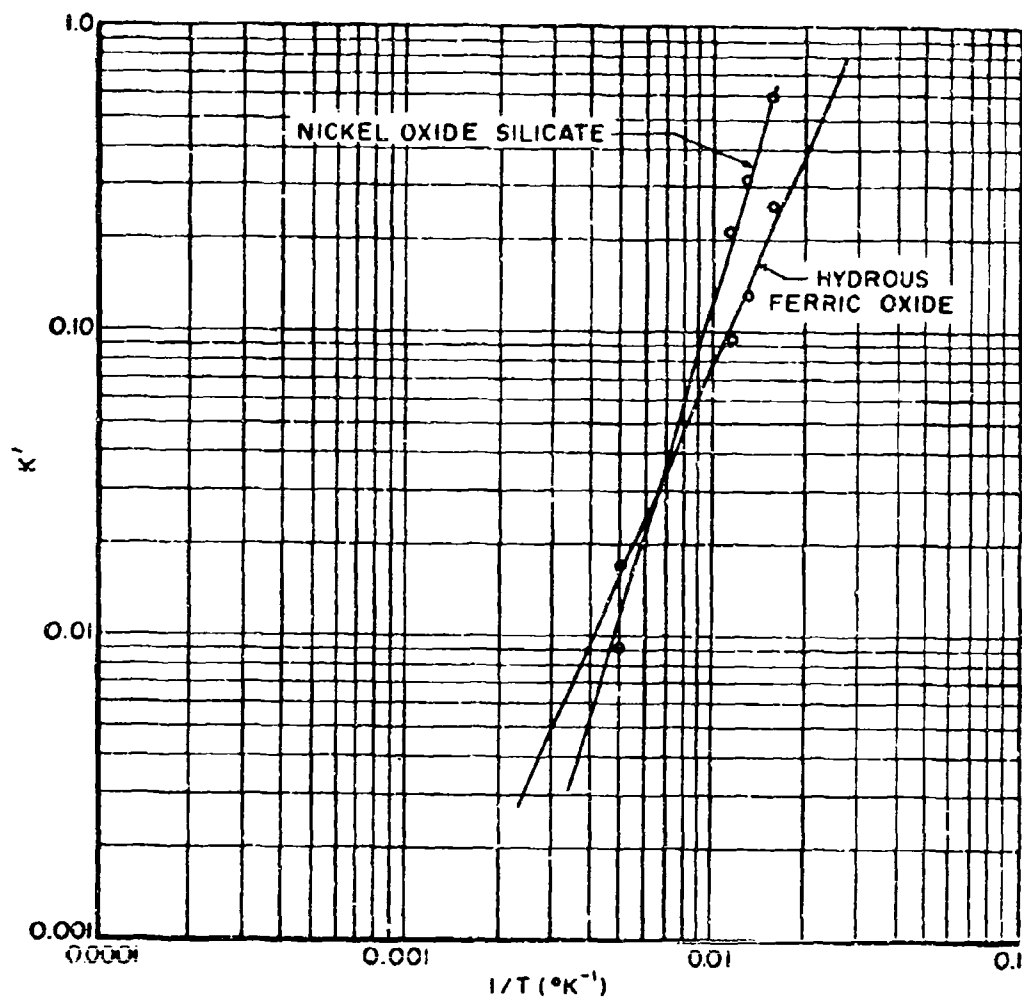


Figure 7. Effect of Temperature on the Constant K'

TABLE XI
ADSORPTION ISOTHERMS FOR HYDROGEN

Hydrous ferric oxide gel adsorbent		
(°K)		
-63.16	C_{H_2}	$= \frac{1.0(p_{H_2})^{2/5}}{1 + (0.26)(p_{H_2})^{2/5}}$
-77	C_{H_2}	$= \frac{5.12(p_{H_2})^{2/5}}{1 + (0.13)(p_{H_2})^{2/5}}$
-87.8	C_{H_2}	$= \frac{3.65(p_{H_2})^{2/5}}{1 + (0.10)(p_{H_2})^{2/5}}$
-194.6	C_{H_2}	$= \frac{0.65(p_{H_2})}{1 + (0.17)(p_{H_2})}$
Nickel oxide/silicate adsorbent		
(°K)		
-63.16	C_{H_2}	$= \frac{56.95(p_{H_2})^{2/5}}{1 + (0.60)(p_{H_2})^{2/5}}$
-77	C_{H_2}	$= \frac{29.91(p_{H_2})^{2/5}}{1 + (0.31)(p_{H_2})^{2/5}}$
-87.8	C_{H_2}	$= \frac{20.10(p_{H_2})^{2/5}}{1 + (0.21)(p_{H_2})^{2/5}}$
-194.6	C_{H_2}	$= \frac{0.76(p_{H_2})}{1 + (0.01)(p_{H_2})}$

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1. ORIGINATING ACTIVITY (Corporate name)		20. REPORT SECURITY CLASSIFICATION	
Air Force Aero Propulsion Laboratory Research and Technology Division Wright-Patterson Air Force Base, Ohio		UNCLASSIFIED	
2. REPORT TITLE			
BETTER ROLE OF ADSORPTION IN THE CATALYTIC PARA-ORTHO-HYDROGEN CONVERSION.			
3. DESCRIPTIVE NOTES (Type of report and/or studies on dates)			
(9) Technical report			
4. AUTHOR(S) (Last name, first name, initial)			
Lander, Herbert R.			
5. REPORT DATE		70. TOTAL NO. OF PAGES	70. NO. OF REFS
January 1967		23	2
6. CONTRACT OR GRANT NO.		20. ORIGINATOR'S REPORT NUMBER(S)	
AF-3048		AFAPL-TR-66-142	
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13. ABSTRACT			
Adsorption isotherms of the form			
$C_A = \frac{L'K'(P_A)^n}{1 + K'(P_A)^n}$			
were determined for two para-ortho-hydrogen conversion catalysts, hydrous ferric oxide gel and nickel oxide silicate, at temperatures from 65° K to 195° K and at pressures from 1 to 10 atmospheres.			
For the catalysts studied, Langmuir's isotherm holds at 194.6° K, while at lower temperatures (approximately 60-90° K), the adsorption mechanism appears to be one where two molecules are adsorbed on five effective centers.			
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